

## Tuning Emissive States in Electrogenerated Chemiluminescence

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**Abstract:** Electrogenerated chemiluminescence (ECL) arising from the reaction of radical ions has previously been shown to arise from a variety of states including excited singlets, triplets, excimers, and exciplexes. In this work we describe two systems that form emissive states in ECL with different properties than those when formed with photoluminescence. The first system involves the reaction of the anthracene radical anion with the radical cation of 4,*N,N*-trimethylaniline. ECL from this system exhibited an exciplex whose energy and intensity relative to the emission from the anthracene singlet could be tuned by adjusting the solvent permittivity and ionic strength. Under conditions considered extreme for electrochemical experiments, no added electrolyte in dimethoxyethane, the relative intensity of the anthracene-related exciplex, formed from the encounter complex, was 8 times greater and red-shifted from that generated by photoluminescence in the same solution with 100-fold exciplex partner added. In the second system examined, the benzophenone radical anion reacted with the radical cation of either phenoxathiin or 4-methoxythioanisole; the ECL emission was from the benzophenone triplet state and an excimer. The excimer, a species not seen with photoluminescence, predominated as the benzophenone concentration was elevated into the low millimolar range. The results from these two simple systems clearly demonstrate that the radical ion annihilation pathway of ECL can generate different emissive states than those formed following photoexcitation.

### Introduction

Transient, excited state, dimeric complexes can be classified as exciplexes (heterodimers) or excimers (homodimers).<sup>1</sup> Most commonly formed from planar reagents whose pi systems can closely interact, these complexes occur because of their enhanced stability in the excited state; ground states of these complexes are typically unstable, and upon relaxation, the molecules dissociate. This unstable ground state leads to a characteristic featureless emission. Exciplexes can be distinguished from excimers because the emission wavelength varies with the local dielectric, having greater energy in environments of low permittivity. There is interest in studying these states because of their relationship with the encounter complex and for their potential use in organic light emitting diodes (OLED's),<sup>2-4</sup> but these states are not generated to a great extent in traditional photochemistry.

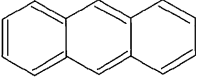
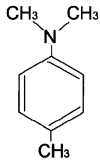
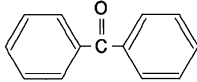
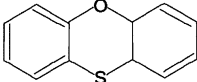
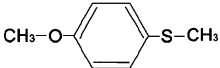
Chemiluminescence (CL), emission arising from chemical reactions, allows generation of a variety of emissive states that cannot be populated photochemically. Electrogenerated chemiluminescence (ECL), which arises following chemical reactions of reagents generated by redox processes at electrodes,<sup>5,6</sup> is a

particularly convenient way to form such states. In both CL and ECL, electronically excited states can be populated by electron-transfer reactions rather than promotion by photonic excitation. ECL arising from excited triplets,<sup>7,8</sup> as well as ECL and CL formation of excited-state complexes such as excimers and exciplexes,<sup>9-14</sup> are all examples of emission from states that are not directly formed photochemically. However, the ability to control and tune these processes by altering the solution conditions is a feature of chemiluminescence that has been insufficiently explored. Since production of excited states by electric fields in the solid state has been shown to follow similar pathways as those in solution,<sup>6,15,16</sup> the ability to control formation of emissive states is important not only in ECL but also in the design of OLED's.

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Chart 1

Radical Anions	Radical Cations
<b>Anthracene (AN)</b> 	<b>4,N,N-Trimethylaniline (TMA)</b> 
<b>Benzophenone (BP)</b> 	<b>Phenoxathiin (PX)</b> 
	<b>4-Methoxythioanisole (4-MTA)</b> 

ECL has been traditionally studied with only slight modifications to conventional electrochemical apparatus. However, the use of microelectrodes for ECL generation allows significant improvements in these measurements.<sup>17</sup> The reduced ohmic drop with microelectrodes allows a variety of solution conditions to be explored. When the microelectrode is used in a flow injection analysis system, multiple solutions can be directed past the electrode allowing rapid evaluation of ECL under a variety of solution conditions. Furthermore, microelectrodes, with their low time constant, allow for short time scale experiments, enabling many side reactions to be outrun and allowing light generation from relatively unstable radicals. The use of electrochemical cells with a narrow gap between opposing electrodes provides another way to minimize the time between electrogeneration and the annihilation reaction.<sup>18</sup> Using these approaches, we have been able to examine ECL from states not populated in photoluminescence (PL)<sup>8</sup> and to generate highly intense emissive states.<sup>19</sup> Here we use it to examine and tune ECL from excimers and exciplexes that arise, in part, from the encounter complex in which electron transfer occurs.

A classic example of an exciplex, known from PL, is the pairing of anthracene (AN, Chart 1) with *N,N*-dimethylaniline.<sup>20</sup> While this pair is unsuitable for ECL investigation because of instability of the radical cation of *N,N*-dimethylaniline, AN in the presence of 4,*N,N*-trimethylaniline (TMA, Chart 1) was found to form a similar exciplex. The presence of a methyl group at the para position of TMA stabilizes the radical cation, allowing its use in ECL experiments. Here we show that reaction of the AN radical anion with the TMA radical cation generates an exciplex via electron transfer that has quite different properties from those formed photochemically. In addition, we examine ECL from benzophenone (BP, Chart 1). Photoluminescence of BP is unusual in that it is from an excited triplet state. When the excited state is generated via ECL by reaction

between the BP radical anion and the radical cation of either phenoxathiin (PX, Chart 1) or 4-methoxythioanisole (4-MTA, Chart 1), a second emissive state is also seen. In both of these systems we find that unique emissive states can be tuned by the solution conditions.

## Experimental Section

**Apparatus.** ECL experiments were conducted in a flow injection apparatus that has been described previously.<sup>17</sup> Briefly, a syringe pump delivers the mobile phase through a 500  $\mu\text{L}$  loop injector that has pneumatic actuation. The solution is then directed to an electrochemical cell that has a channel geometry. The cell contains a microelectrode and silver band quasi-reference electrode (QRE) embedded in epoxy on one side of the channel and a quartz window on the opposite side. A thin (200  $\mu\text{m}$ ) Teflon gasket determines the thickness of the channel. The potential waveform was generated with a function generator (Hewlett-Packard 33120A). Electrochemical current was monitored with a fast current to voltage converter (built in house), and an oscilloscope (Tektronix TDS 380) was used to monitor the signals. ECL transients were detected with a PMT (Hamamatsu R1878) connected through a fast preamp to a multichannel scaler (EG&G-Ortec Turbo-MCS). Long pass and short pass absorption glass filters (Chroma) were used to isolate emissions occurring at different wavelengths. ECL spectra were obtained with a fiber optic based spectrometer (Ocean Optics S2000-FL). Photoluminescence spectra were obtained with a Jobin Yvon FluoroLog fluorimeter with slits set for 1 nm resolution.

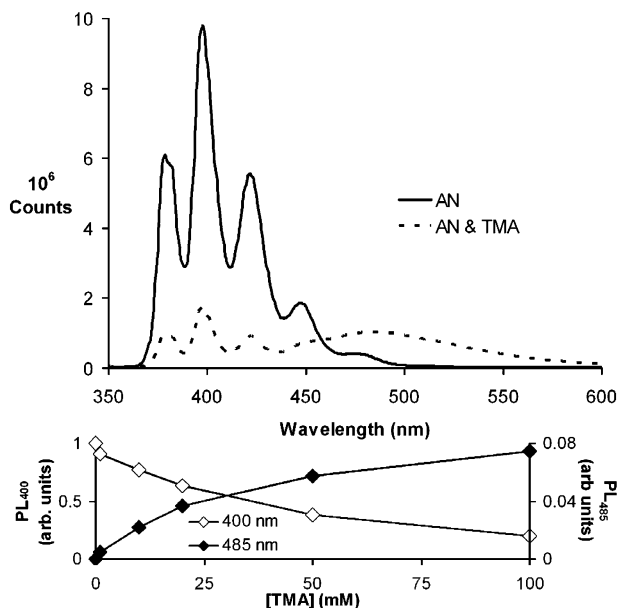
**Procedures.** All experiments were done with a flow rate of 33  $\mu\text{L}/\text{min}$ . Solutions were injected with the pneumatic valve, and cyclic voltammetry (80 V/s) was used to determine the potentials for generation of ECL ( $\sim 300$  mV beyond the  $E_{1/2}$  values). ECL was generated with double potential-step chronoamperometry (5 ms steps) with the anodic step first. The electrode was maintained at 0.0 V for 90 ms between the double potential steps so that reagents generated during one potential-step sequence would not affect the next one. Light was monitored by photon counting during the reducing step and for 5 ms afterward. Collected light was binned at 10  $\mu\text{s}$  intervals. Emission from multiple cycles (typically 100) was summed to improve signal-to-noise. For the collection of spectra, ECL was generated with a potential square wave at the frequency where emission was maximal (from 40 to 400 Hz depending on solution conditions).

**Thin Layer ECL.**<sup>18</sup> A thin layer cell with two opposing electrodes was used for DC generation of ECL. A gold square (5 mm  $\times$  7 mm  $\times$  2 mm thick) was embedded in epoxy and polished to form one side of the cell. The opposing side was an optically transparent indium tin oxide (ITO) coated glass. The electrodes were separated with a 3.4  $\mu\text{m}$  thick Mylar spacer. The potential difference applied between the two electrodes was set to cause oxidation at the ITO electrode and reduction at the gold electrode.

**Chemicals.** Acetonitrile (Fisher) and dimethoxyethane (DME, Fisher) were dried before use with activated alumina. The DME was checked for peroxides before use. Phenoxathiin (PX, Aldrich) and anthracene (AN, Aldrich) were recrystallized twice from ethanol. 4,*N,N*-Trimethylaniline (TMA, Fluka), benzophenone (BP, Fluka), and tetrabutylammonium hexafluorophosphate (TBAH, Fluka) were obtained at high purity  $\geq 99\%$ . BP and TBAH were dried in a vacuum oven before use. Solutions contained 0.1 M TBAH, except where noted, and were deoxygenated by bubbling with dry  $\text{N}_2$ .

4-Methoxythioanisole (4-MTA) was synthesized from methyl iodide (Fisher) and 4-methoxybenzenethiol (Aldrich). The reaction was carried out in tetrahydrofuran (THF) at room temperature with triethylamine and calcium bicarbonate present to facilitate deprotonation and to remove  $\text{H}^+$  from solution. The product was purified after evaporating the THF, by extraction into dichloromethane from water followed by rotary evaporation of the dichloromethane phase. NMR showed product only.

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**Figure 1.** (Top) PL spectra of 1.0 mM AN in cyclohexane containing 0 mM TMA (—) or 100 mM TMA (---); excitation at 338 nm. (Bottom) PL intensity as a function of [TMA]. The exciplex emission increases while the singlet emission decreases.

**Table 1.** PL and ECL Data for AN/TMA System<sup>a</sup>

solvent	electrolyte (mM TBAH)	generation method	<sup>1</sup> AN* (nm)	Ex* (nm)	rel intensity (Ex*/ <sup>1</sup> AN*)
cyclohexane	0	PL	400	485	0.38
DME	0	PL	400	567	0.18
DME	100	PL	400	597	0.039
DME	0	ECL	400	580	1.5
DME	1	ECL	400	589	0.62
DME	10	ECL	400	598	0.33
DME	100	ECL	400	613	0.1
acetonitrile	0	PL	400	600 ≤ λ <sub>max</sub> ≤ 620	≤0.008
acetonitrile	100	ECL	400	610	0.07

<sup>a</sup> PL is all 1 mM AN 100 mM TMA. ECL is 1 mM each AN and TMA.

## Results

**PL of Anthracene with TMA.** In cyclohexane, as in acetonitrile and DME, PL spectra of 1 mM AN excited at 338 nm shows fluorescent emission at 400 nm from AN (Figure 1, top; Table 1 summarizes all spectral data for ECL and PL experiments with the AN/TMA system). With TMA present in concentrations ranging from 0.1 to 100 mM, the fluorescence from AN in cyclohexane decreases with increasing [TMA], and a broad emission at 485 nm grows in (Figure 1, bottom). The emission has a visible change in color from violet for pure AN to blue for AN/TMA mixtures. The luminescence of the TMA/AN system is similar to that of the *N,N*-dimethylaniline/AN system that is known to form an exciplex.<sup>20</sup> Exciplex emission generated by PL from TMA/AN mixtures in acetonitrile ( $\epsilon = 37.5$ ) is much weaker than in cyclohexane ( $\epsilon = 2$ ) and red shifted past 600 nm. Dimethoxyethane ( $\epsilon = 7.5$ ), with an intermediate dielectric constant, has an intermediate exciplex emission generated by PL with a maximum at 570 nm. The quenching of AN fluorescence caused by TMA is similar in acetonitrile and DME to that in cyclohexane.

**ECL from AN/TMA Solutions.** In dry acetonitrile containing 0.1 M TBAH, anthracene is reduced in a reversible, one-electron process at  $E_{1/2} = -1.78$  V vs Ag QRE, and TMA is oxidized

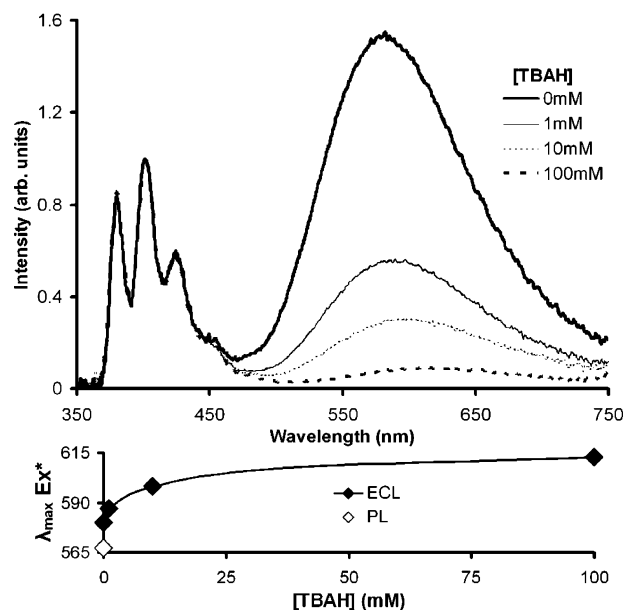
in a one-electron process at  $E_{1/2} = 0.98$  V vs Ag QRE. Annihilation of the radical anion of anthracene and the radical cation of TMA yields sufficient free energy (ca. 2.7 eV) to form anthracene's triplet excited state (1.82 eV) but not enough to form the singlet (3.28 eV). However, triplet-triplet annihilation (TTA) allows formation of the excited singlet state.<sup>21</sup> Indeed, the ECL from the reaction of the radical ions generated with double potential step chronoamperometry has a maximum at 400 nm, and the features in this wavelength region are identical to the photoluminescence.

Of greater interest in the present study are the properties of the broad ECL emission with  $\lambda_{\max} = 610$  nm that resembles the exciplex emission obtained during PL. The intensity of this emission, relative to the singlet emission, when generated with equal (1 mM) concentrations of AN and TMA in acetonitrile was greater than the relative emission generated by PL with 100 mM TMA and 1 mM AN in the same solvent (Table 1). In DME, cyclic voltammetry reveals that the energy available from the annihilation reaction is quite similar to that in acetonitrile. ECL of this system in DME containing 100 mM TBAH also has emission at 400 nm accompanied by a similar long wavelength component at 610 nm. Note that this peak is considerably red shifted in comparison to the PL exciplex emission in DME, and its intensity relative to the singlet emission is also greater (Table 1).

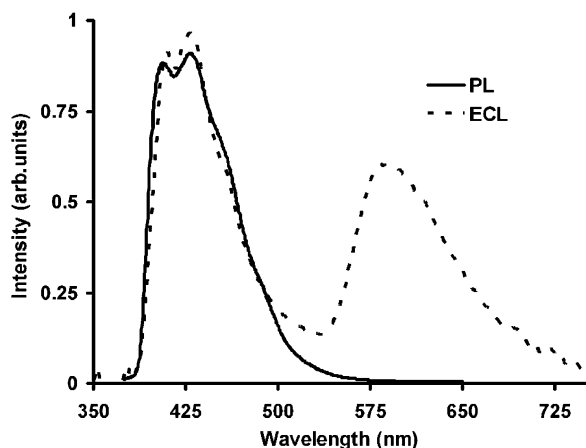
**Electrolyte Effects on AN/TMA ECL.** The only difference in the solutions used for PL and ECL is the presence of TBAH as a supporting electrolyte. Therefore, we added 100 mM TBAH to the DME solutions and examined the PL. The salt lowered the exciplex emission to ca. 15% of the original intensity and shifted the emission maximum from 567 to 597 nm. To investigate the role that TBAH plays on the emission in ECL, potential step experiments were attempted in DME with low electrolyte concentrations. Even with a microelectrode the large ohmic drop caused equivocal results. Therefore, ECL was generated with a DC potential in a thin layer cell with dual opposing electrodes. In such a cell, the current at the anode and cathode must be equal. Since the area of the ITO was greater than the gold cathode, the current density at the gold was greater resulting in a higher concentration of AN<sup>•-</sup>. So long as the bulk concentration of AN was less than or equal to the TMA concentration, the potential difference applied between the two electrodes (3.2 V) could be maintained so that solvent electrolysis and oxidation of AN did not occur. With this approach, we examined ECL spectra in DME at different concentrations of supporting electrolyte.

The spectral position of the ECL from the singlet-excited state of AN in DME did not vary with TBAH concentrations from 0 to 100 mM (Figure 2, top). The intensity of the singlet-state emission decreased slightly with decreasing [TBAH], but this was within the experimental error of these experiments. However, as [TBAH] was decreased, the long wavelength emission blue shifted and the intensity relative to the singlet-state emission increased (Figure 2, Table 1). Relative peak intensities for the exciplex emission to the singlet emission ( $Ex^*/^1AN^*$ ) increased 15-fold with no added supporting electrolyte compared to the intensity with 100 mM TBAH. The peak of

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**Figure 2.** (Top) ECL exciplex emission behavior in DME with TBAH concentrations of 100 mM, 10 mM, 1 mM, and 0 mM, relative to the AN\* emission. ECL was generated with a thin layer cell. (Bottom) Wavelength maxima for the exciplex as a function of electrolyte concentration. The open diamond gives the exciplex wavelength maximum in PL of salt free DME containing 1 mM AN and 100 mM TMA.

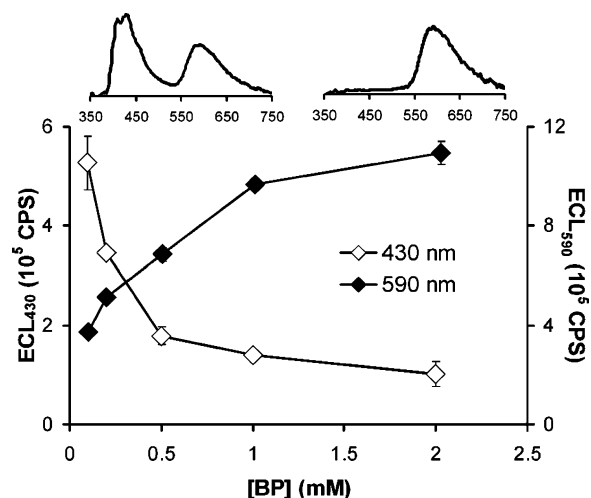


**Figure 3.** Luminescence spectra of BP in the presence PX. ECL (---) is from an acetonitrile solution containing 2.0 mM PX and 0.1 mM BP generated with a 400 Hz square wave at a microelectrode. PL (—) is from 0.1 mM BP in deoxygenated acetonitrile with excitation at 355 nm.

the exciplex emission shifted from 613 to 598 nm to 589 nm and, in electrolyte free solution, was centered at 580 nm (Figure 2, bottom).

**PL and ECL of Benzophenone.** Photoluminescence of BP in acetonitrile with excitation at  $\lambda = 355$  nm shows emission with a maximum at 430 nm (Figure 3). The emission was identical in cyclohexane where prior measurements have shown the emission is from the excited triplet state of BP.<sup>7</sup> Consistent with this assignment, the PL emission from BP was quenched by O<sub>2</sub>. The emission spectra was unchanged upon addition of PX or MTA or electrolyte (TBAH).

Reduction of BP in acetonitrile containing 0.1 M TBAH is a one-electron process at  $E_{1/2} = -1.85$  V vs Ag QRE. The oxidations of both phenoxathiin and 4-MTA in this solution are one-electron processes occurring at  $E_{1/2} = 1.17$  V and  $E_{1/2} = 1.15$  V, respectively, vs Ag QRE. Both PX and 4-MTA



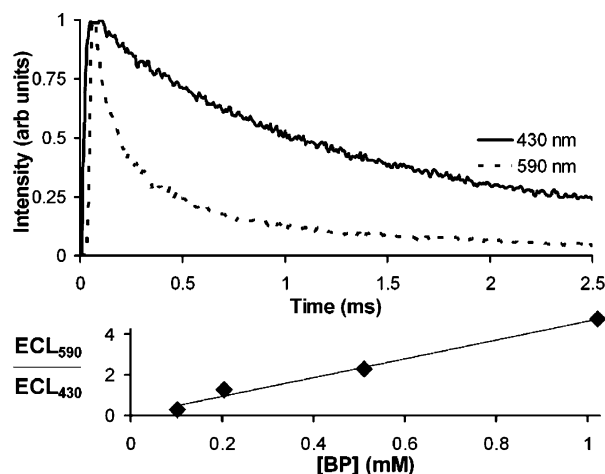
**Figure 4.** Dependence of ECL emission on BP concentration at 430 and 590 nm with [PX] at 5 mM. Intensities were measured during the potential step (5 ms duration) that resulted in BP reduction. Double potential step sequences were repeated at 50 ms intervals. Above spectra were taken with 0.1 mM BP (left) and 2 mM BP (right), the 2 mM BP collection was too short to see <sup>3</sup>BP\* emission.

exhibit second oxidation waves that move negative in the presence of water; to prevent this, solutions were rigorously dried before experiments. Reaction of the BP radical anion and the radical cation from either PX or 4-MTA yields sufficient energy (ca. 3.0 eV) to form <sup>3</sup>BP\* (2.99 eV).<sup>7</sup> The energies for <sup>1</sup>BP\* (3.22 eV),<sup>7</sup> <sup>1</sup>PX\* (>3.3 eV, as estimated from its absorbance spectra), and the singlet of 4-MTA, which is at higher energy than <sup>1</sup>PX\*, are inaccessible.

In a solution containing equal concentrations of BP and PX, stable ECL was observed during both steps of a square wave. A spectrum of the ECL has a maximum at  $\lambda_{\text{max}} = 430$  nm, consistent with the PL spectra, but also has emission at longer wavelengths with  $\lambda_{\text{max}} = 590$  nm (Figure 3). Emission at an identical wavelength was observed with 4-MTA serving as the radical cation. Previously, Bard and co-workers examined this system and suggested a possible source of the long wavelength emission as decomposition product(s) from the radical ions.<sup>7</sup> This seems unlikely in these experiments with microelectrodes where the reagents were only generated for a few milliseconds and the contents of the electrochemical cell were purged in the relatively long time between potential steps by the solution flow. Furthermore, cyclic voltammograms obtained immediately following ECL and with the flow stopped showed neither the loss of reagents nor the presence of new species.

**Effect of Reagent Concentrations.** The relative intensities of the two emission maxima in the ECL spectra varied differently with the concentration of BP. As the concentration of BP was increased from 0.1 mM to 2 mM in acetonitrile, with the concentration of PX at 5 mM, the ECL intensity of the 590 nm emission grew while the 430 nm emission decreased (Figure 4). In contrast, varying the concentration of PX from 0.1 to 2.0 mM with 5 mM BP yielded ECL in which both the 590 and 430 nm emissions increased, although the 430 nm emission was very weak for all concentrations of PX. At high concentrations of BP (5 mM), the ECL from a 30  $\mu\text{m}$  radius disk is visible to the naked eye as an orange glow (<sup>3</sup>BP\* emission would be blue). Similar variation in emission intensities were observed when 4-MTA was substituted for PX. In addition,





**Figure 5.** (Top) Normalized ECL intensities of the 430 nm (—) and 590 nm (---) emissions as a function of time. (Bottom) Plot of the ratio of 590 nm to 430 nm emission as a function of [BP].

the emission was from identical wavelengths in DME containing 100 mM TBAH.

To gain further insight into the long wavelength emissive species, the decay rates of the ECL at each wavelength were examined. During the second potential step, emission at 590 nm decayed more rapidly than that at 430 nm (Figure 5, top). Emission during ECL decays because the reagent generated on the previous step is either consumed by electrolysis or reaction or diffuses away from the reaction zone.<sup>22</sup> Taking a ratio of the intensities at a specific time during the ECL decay removes factors that the two pathways have in common. The counts 2.5 ms into the second potential step were collected, and the ratio of the intensities ( $I_{590}/I_{430}$ ) plotted versus [BP] was found to be linear (Figure 5, bottom). This indicates that the formation of each state differs in that the reaction order of BP (in any of its possible forms) is one greater for the 590 nm emission than it is for the 430 nm emission (i.e., second order vs first order in [BP]).

## Discussion

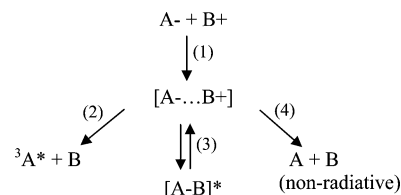
The intensities of excimers and exciplexes generated by PL, as well as the emission wavelength of exciplexes, are known to be affected by the solvent permittivity and the presence of ions. The results of this study demonstrate that excited states formed via ECL are subject to these same interactions, but they also reveal that additional factors can direct the observed emission. The differences between PL and ECL generation of excited states are due to the radical-ion encounter complex that is central in the formation of ECL emissive states, its sensitivity to the presence of ions, and the presence of radical reagents in ECL reactions. In the AN/TMA system, the encounter complex formed during ECL promotes a greater population of exciplexes. In the BP system, the presence of radicals during ECL leads to a completely new emissive state. An understanding of the factors that control ECL emission allows it to be tuned by the concentration of supporting electrolyte, the permittivity of the solvent, and the concentration of reagents.

In PL, exciplexes are formed when an excited-state molecule encounters another molecule with which it can form a close

association. The aromatic components of AN and TMA allow them to form such an association. Exciplexes generated by CL become more intense and shift to higher energies in solvents of low permittivity<sup>11,23</sup> because the solvent's ability to stabilize polar molecules and ions is decreased and the associated complexes form exciplexes without dissociation to other products. Thus, in acetonitrile, a solvent with a relatively high dielectric constant compared to cyclohexane and DME, association of TMA with the excited singlet of AN occurs and leads to quenching of the singlet emission, but exciplex emission is quite low. The supporting electrolyte concentration also affects PL from the exciplex. The wavelength of exciplex emission is governed by the free energies of the molecules in the exciplex and its solvation. Because an exciplex has a dipole, ions will associate with it, affecting solvation and causing a red shift as electrolyte is added. The electrolyte also alters the associated complex so that a contact ion pair is favored rather than the exciplex, and the PL intensity is diminished. In some cases, full electron transfer can occur within this complex to produce radical ions.<sup>24–27</sup>

Exciplexes generated by ECL have been shown to exhibit a similar solvent dependence. For example, the exciplex emission from the dibenzoylmethane/tri-*p*-tolylamine system decreases in intensity and emission wavelength with increased permittivity of the solvent.<sup>13</sup> However, as shown here, the different route to exciplex formation in ECL can dramatically alter the energy and abundance of exciplexes. Scheme 1 illustrates the pathways in ECL. The primary reaction 1 involves the radical ions coming together to form an encounter complex  $[AN^{\cdot-}\dots TMA^{+\cdot}]$ . This complex can undergo electron transfer yielding the AN excited triplet (reaction 2), form an excimer  $[AN-TMA]^*$  (reaction 3), or decompose by a nonradiative pathway, (reaction 4).

## Scheme 1



Even though reaction 4 is ongoing in acetonitrile, the AN/TMA exciplex is formed, and to a greater degree during ECL as compared to PL. This forced interaction in reaction 1 leads to a greater likelihood of seeing emission from an exciplex compared with PL where  ${}^1AN^*$  can emit without ever encountering a TMA molecule. In DME with high electrolyte, the exciplex generated by ECL is more intense than that when generated by PL for the same reason.

In DME, however, there is another parameter that affects the exciplex emission: the supporting electrolyte concentration. Table 1 shows that at constant supporting electrolyte concentration in DME, ECL from the excimer is more intense and red shifted when compared to PL. This is a consequence of the effects of the supporting electrolyte on the competing processes

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in Scheme 1. The intensity is greatest in the absence of supporting electrolyte because reaction 1 becomes the predominant pathway to neutralize the charge of the free radical ions. In electrolyte-free DME, the electrolytic reduction/oxidation processes force migration of ions into the diffusion layer where electroneutrality is required<sup>28</sup> and the light emitting reactions occur. For this reason, ECL generated in the absence of supporting electrolyte is still red-shifted from that of the PL. Increasing the concentration of the supporting electrolyte in a low permittivity solvent (like DME) allows increased association of ions and other polar species with electrolyte: the more polar the species, the tighter the association. The effect on the radical ions is seen in the decreased difference between redox potentials of reactions that generate radical anions and cations because the solution conditions more readily allow formation of tight ion pairs with the counterion of the electrolyte.<sup>19</sup> The encounter complex is similarly affected, as electrolyte ions become associated with the highly polar complex. Thus, when the supporting electrolyte is raised, the radical ions in the encounter complex are less closely associated, and the equilibrium that exists between the encounter complex and the exciplex shifts away from the exciplex. Because of both the shift in equilibrium and the fact that electron transfer can occur to form AN\* at greater distances than are necessary for exciplex formation, less exciplex is formed. Exciplexes that do form and emit in this environment are still associated with electrolyte ions, to a greater extent than in PL, and the greater red shift is the result of these ions lowering the energy of the excited complex.

The presence of the electrogenerated, reactive radicals can affect ECL spectra beyond simple ion association. ECL from the BP systems examined in this work shows an emissive state at 590 nm that is not present in our PL spectra. The ECL results show that the long wavelength emission is present in both acetonitrile and DME. Furthermore, it increases in intensity with [BP] relative to the triplet state whereas both increase when the radical cation concentration is increased. This ECL behavior is similar to the formation of the exciplex at the expense of the singlet emission seen in the PL of the AN/TMA system (compare Figure 1 bottom with Figure 4). In the PL system, the TMA concentration dependence is due to the competition between emission from AN\* and quenching or exciplex formation by association with TMA. During ECL, an analogous competition is involved in the quenching of the BP triplet and the increase of the 590 nm emission. Indeed, the long lifetime of the BP triplet<sup>29</sup> allows its conversion to another product before relaxation to the ground state. Furthermore, the energetics of the encounter complex that leads to ECL ensures that the only excited state that can be directly formed is the BP triplet. Therefore, the long wavelength emissive state that predominates during ECL generation must arise from a BP species that is not present in PL solutions, that is, its radical anion.

Using intense lasers, Naqvi and Wild were able to generate a similar (577 nm) emissive state from BP.<sup>30</sup> Based upon its dependence on protic solvents and high intensity radiation, they ascribed the emission to an excited state of the BP radical, which could be obtained photochemically. The excited state BP radical itself is not energetically accessible by direct electron transfer

and, in ECL, cannot be photoexcited, but it could be formed via fluorescence resonance energy transfer (FRET) or reabsorption. While these cannot be eliminated as source mechanisms, they are unlikely. First, the concentration of the radical anion, though relatively high, is still rather low for substantial FRET. Second, using a microelectrode and short potential pulses, the volume of solution occupied by BP<sup>•-</sup> is very small (<100 pL), so that the path length for reabsorption is very small.

Figure 5 shows that the reaction order of BP is one greater for this emissive state than it is for the <sup>3</sup>BP\* emission. Because the reactions preceding and including formation of the encounter complex must be the same for both emissions, the additional BP must be involved sometime at or after its formation. Discounting FRET as a possibility, the evidence from our ECL experiments leads us to propose the emission is from an excimer. Excimers can form via reactions between an excited state and ground-state molecule (reaction 5), through the TTA pathway (reaction 6),<sup>31</sup> or from an interaction between an excited state and a radical (reaction 7):



All three of these reactions would exhibit a higher reaction order in BP than the pathway involving direct triplet formation, consistent with the data. However, reactions 5 and 6 represent situations that can and do exist in PL studies, but PL spectra of BP, even at high concentrations, do not exhibit the long wavelength emission, except for that seen with very intense radiation by Naqvi and Wild. Furthermore, reaction 6 represents a case that would produce increased intensities of both the excimer and the triplet emissions with increasing [BP]. ECL produces an environment where both BP and BP<sup>•-</sup> exist, promoting reaction 7, and generating a condition that does not exist in typical PL. Even if BP<sup>•-</sup> were present during PL, it absorbs much more strongly than BP at the BP excitation wavelength (>100× greater molar absorptivity),<sup>32</sup> making interactions between BP\* and BP<sup>•-</sup> difficult to ascertain. Typically triplet-radical encounters result in quenching, but as the radical in this case is also BP, and the energy of the triplet state is so high, any nonradiative pathway would still involve a highly exothermic step that would, like ground-state formation from the encounter complex, lie in the Marcus inverted region. Reaction 7 can lower the intensity of BP\* while promoting long wavelength emission if the rate is sufficiently fast compared to triplet emission.

Park and Bard observed similar ECL from BP using the radical cation of tri-*p*-tolylamine as a reagent.<sup>13</sup> They attributed the emission to an exciplex, since the enthalpy of the radical ion reaction was insufficient to form the triplet directly. However, in our experiments the 590 nm emission is unlikely to arise from an exciplex because the emission wavelength is independent of reaction partner. Furthermore, the relative intensity of the two peaks is independent of the concentration of the radical cation precursor. Emission from an excited state

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of the BP radical anion reaction partner (i.e.,  $^3\text{PX}^*$  or  $[\text{PX}-\text{PX}]^*$ ) is ruled out because replacement of PX with the structurally dissimilar 4-MTA leads to ECL with BP that is identical in emission wavelength and concentration dependence.

### Conclusions

The annihilation reaction between a radical cation and anion proceeds under conditions that allow the creation and control of unusual excited states. The first intermediate in the annihilation reaction is the encounter complex. The energy of this complex is tied to those of the radicals that precede it, and all these, along with some emissive states that can follow, are strongly affected by their environment. As demonstrated, the medium permittivity, the ionic concentration, and concentration of reagents can all be adjusted or chosen so as to tune the reaction rates and equilibria, and these effects are manifested in the emission energy and the overall ECL efficiency.<sup>19</sup> The ECL emission is spatially confined to a relatively thin plane some distance away from the electrode. Within the region of this plane are found the electrogenerated species and any excited state(s) that have already formed, all in relatively high concen-

trations. This allows their cross reactions that result in the multiple emissive states that can be formed.

These effects on ECL in solution can be used to predict the behavior in solid state devices such as OLEDs. OLEDs normally do not contain ionic species and typically have very low permittivity ( $\epsilon \approx 2$ ). Because diffusion does not occur, and negative (electrons) and positive (holes) species are usually in different layers, the possibility of association with other charges is limited to the interfacial region. Our finding of a high rate of exciplex formation in a low permittivity, low conductance environment would predict very bright exciplex emission occurring high energies. With such an environment, molecules "locked" in place in low permittivity polymers ( $\epsilon \approx 2$ ), this is precisely what is seen in OLEDs.<sup>2-4</sup>

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